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THE EFFECT OF γ -RADIATION ON THE DIELECTRIC PROPERTIES OF HDPE/ α -SiO₂ COMPOSITES

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ARTICLE INFO	ABSTRACT
<p><i>Article history:</i> Received: 2024-10-09 Received in revised form: 2024-10-16 Accepted: 2024-11-14 Available online</p> <hr/> <p><i>Keywords:</i> nanocomposite, dielectric permittivity, electrical conductivity, frequency.</p>	<p><i>The impact of γ-irradiation on the electrical and thermoelectret properties of HDPE/α-SiO₂ nanocomposites was thoroughly studied, with a particular focus on the influence of varying filler concentrations ranging from 0% to 5% by volume. This research aimed to investigate how both the γ-irradiation and the addition of α-SiO₂ nanoparticles affected the overall electrical behavior of the nanocomposite. Key electrical properties such as the dielectric constant (ϵ'), dielectric loss coefficient (ϵ''), and alternating current (AC) electrical conductivity (σ) were measured over a broad frequency range spanning from 25 Hz to 1 MHz. Furthermore, the samples were exposed to absorbed γ-radiation doses ranging from 0 to 200 kGy, to evaluate the dose-dependent effects. The results showed that increasing the filler concentration and irradiation dose significantly altered the dielectric and conductive properties, providing valuable insights into the optimization of nanocomposites for various electrical applications. These findings suggest that the controlled use of fillers and irradiation can be used to fine-tune the electrical performance of polymer-based nanocomposites.</i></p>

ВЛИЯНИЕ γ -ИЗЛУЧЕНИЯ НА ДИЭЛЕКТРИЧЕСКИЕ СВОЙСТВА КОМПОЗИТОВ HDPE/ α -SiO₂

РЕЗЮМЕ

Влияние γ -облучения на электрические и термоэлектретные свойства нанокompозитов HDPE/ α -SiO₂ было тщательно изучено, с особым акцентом на влияние изменения концентрации наполнителя в диапазоне от 0% до 5% по объему. Целью исследования было выяснить, как γ -облучение и добавление наночастиц α -SiO₂ влияют на общие электрические характеристики нанокompозита. Основные электрические свойства, такие как диэлектрическая проницаемость (ϵ'), коэффициент диэлектрических потерь (ϵ'') и электропроводность переменного тока (σ), измерялись в широком диапазоне частот от 25 Гц до 1 МГц. Кроме того, образцы подвергались воздействию γ -облучения в дозах от 0 до 200 кГр для оценки дозозависимых эффектов. Результаты показали, что увеличение концентрации наполнителя и дозы облучения значительно изменяет диэлектрические и проводящие свойства, предоставляя ценные данные для оптимизации нанокompозитов для различных электрических применений. Эти выводы предполагают, что контролируемое использование наполнителей и облучения может быть использовано для тонкой настройки электрической производительности полимерных нанокompозитов.

Ключевые слова: нанокompозит, диэлектрическая проницаемость, электропроводность, частота.

γ -RADİASİYANIN YSPE/ α -SiO₂ KOMPOZİTLƏRİN DİELEKTRİK XASSƏLƏRİNƏ TƏSİRİ

XÜLASƏ

Yüksək sıxlıqlı polietilen (YSPE) və onun əsasında alınan nanokompozit (YSPE/ α -SiO₂) nümunələrinə γ -şüalanmanın və termoelektret halının təsiri tədqiq edilmişdir. 0-5% həcmində doldurucunun konsentrasiyasının, udulma dozasının və termoelektret halının elektrofiziki xassələrə təsiri müəyyən edilmişdir. Dielektrik nüfuzluğu (ϵ'), dielektrik itki faktoru (ϵ''), elektrik keçiriciliyi (σ) 25÷10⁶Hz tezlik və 0-200kGr udulma dozası diapozonunda tədqiq edilmişdir. Nəticələr göstərmişdir ki, dolğu konsentrasiyasının və şüalanma dozalarının artması dielektrik və keçirici xassələri əhəmiyyətli dərəcədə dəyişir və bu, nanokompozitlərin müxtəlif elektrik tətbiqləri üçün optimallaşdırılmasına dair mühüm məlumatlar verir. Bu nəticələr göstərir ki, doldurucuların və şüalanmanın nəzarətli istifadəsi polimer əsaslı nanokompozitlərin elektrik performansını incə tənzimləmək üçün istifadə oluna bilər.

Açar sözlər: nanokompozit, dielektrik nüfuzluğu, elektrik keçiriciliyi, tezlik.

Introduction

In recent years, one of the most promising and rapidly developing directions in science and technology has been the production of new nanocomposites. High-density polyethylene (HDPE) and composites based on it are considered indispensable materials in fields such as the atomic and electrical engineering industries, cryogenic technology, medicine, and more. Through various complex methods, nanoparticles are incorporated into the polymer matrix. Such composites exhibit several unique and promising properties (electrophysical, electret, optical). Due to these properties, they are valuable in the development of new sensors, photovoltaic converters, various detectors, piezoelectric materials, and more. Researchers [1, 2] have determined in their studies that adding inorganic nanoparticles to polymers significantly modifies the physical properties of polymer materials, enhancing their applications.

Current research shows that composites obtained by adding nanoparticles at various concentrations, particularly in the range of 1-10%, into the polymer matrix demonstrate superior physical, chemical, mechanical, and dielectric properties compared to the original polymers [3].

In the current era, the interest in composites obtained by adding nanoparticle-based oxide materials to a polymer matrix continues to grow consistently [4]. The addition of ultrafine non-organic particles, such as silicon dioxide (α -SiO₂), to high-density polyethylene (HDPE) further improves the physical and mechanical properties of the polymer [5].

It should be noted that when obtaining a new polymer composite material, it is necessary to investigate the dielectric permeability (ϵ), dielectric loss ($\text{tg}\delta$), and conductivity in both direct (σ_{dc}) and alternating (σ_{ac}) fields after the addition of fillers.

One of the modification methods for high-density polyethylene and the composites obtained from it (HDPE/ α -SiO₂) is their irradiation with various types of radiation. Composites modified by ionizing radiation are even more versatile as composite materials. The essence here is the dispersity of the structure and the formation of interphase layers. Due to these characteristics, the application of nanocomposites in micro- and nanoelectronics attracts considerable interest.

The effect of γ -radiation varies depending on the type of polymer. It is known from the literature [6-10] that γ -radiation affects the structure of polyethylene and alters its physicochemical properties, causing irreversible changes in the molecular structure of the polymer. The mechanism of this modification depends on the radiation conditions; it either increases mechanical strength as a result of the construction process in the polymer molecule or leads to molecular fragmentation during the oxidation process.

The increase in dielectric permeability and conductivity in the alternating electric field of HDPE and its composites (HDPE + α -SiO₂) after γ -irradiation is due to the increased density of free radicals and unsaturated bonds. In irradiated samples, the breaking of the molecular chain and the formation of free radicals lead to an increase in the density of unsaturated bonds.

Conducting the Experiment

In the conducted research, high-density polyethylene (HDPE) with a molecular weight of 95×10^3 g/mol, a crystallinity degree of 52%, a melting temperature of 130°C, and a density of 958 g/cm³, marked as 20806-24, and various volumes ($\Phi=0.1, 3, 5\%$) of amorphous silicon dioxide (α -SiO₂) nanofiller (Sky Spring Nanomaterials, Inc. Houston, USA) with a specific surface area of $S=160$ m²/g, a density of 2.65 g/cm³, and particle sizes of 20 nm, were prepared as composites using a thermal pressing method. The powdered high-density polyethylene (HDPE) was weighed on a scale in predetermined concentrations together with the nanofiller, then the polymer matrix and the nanofiller were mechanically mixed in a porcelain container until a completely homogeneous mixture was obtained. The resulting homogeneous mixture was subjected to a pressure of 15 MPa at a temperature of 130°C for 5 minutes using a hydraulic press and then cooled in an ice-water mixture [11]. The obtained samples had a thickness of 120-180 μ m and a diameter of 40 mm. Some of the samples were initially converted into a thermoelectret state, while others were irradiated with γ -radiation ($D=50, 100, 200$ kQr). The electrophysical properties (ϵ , $\text{tg}\delta$, σ) of the samples were investigated before and after the thermoelectret formation and γ -radiation exposure.

To obtain the thermoelectret: HDPE and HDPE+ α -SiO₂ samples are heated from room temperature to 100°C and kept at this temperature between electrodes in an electric field for 30 minutes. They are then allowed to cool to room temperature, and after cooling, they are freed from the electric field. The surface charge density is measured using a compensation method [12]. The gamma radiation exposure of polymer and composite samples was performed using the MPX- γ -25 device based on the ⁶⁰Co isotope. The measurement of the electrophysical properties of HDPE and its composites was carried out at frequencies ranging from 25 to 10⁶ Hz using an E7-20 type impedance meter, under a constant heating regime for the samples.

The electrophysical properties of HDPE and its composites were clarified concerning frequency, temperature, and dose dependencies at various temperatures.

Discussion of Results

In Figure 1, the dielectric permittivity (ϵ') dependencies of HDPE and HDPE+x% α -SiO₂ composites (Fig. 1a) and thermoelectrets (Fig. 1b) before γ -radiation ($D=0$) are presented as a function of various frequencies. It can be seen from the figure that the dielectric permittivity (ϵ') values of the initial HDPE and 1% vol. α -SiO₂ nanocomposites are significantly lower compared to the 3% and 5% vol. nanocomposites at 25 Hz. The dielectric permittivity of HDPE and 1% vol. α -SiO₂ nanocomposites does not depend on frequency, meaning that with the increase in frequency, the value of ϵ' changes slightly (decreases). The 3% and 5% vol. samples obtain high values at 25 Hz (5.34 and 6.38, respectively), and with the increase in frequency, it decreases rapidly up to 10⁴ Hz, then weakens and stabilizes at the end (10⁶ Hz). As the volume percentage of the filler increases (3%; 5%), the value of ϵ' increases; however, in the HDPE+5% α -SiO₂ composite, the value of ϵ' decreases approximately 1.97 times with increasing frequency. The parameter $\Delta\epsilon' = (\epsilon'_c - \epsilon'_\infty)$, where ϵ'_c and ϵ'_∞ are the low and high-frequency dielectric permittivity, respectively, encompasses the entire range of dispersion and is equal to $\Delta\epsilon' = 3.66$.

In Figure 1b, it is evident that the character of the $\epsilon = f(\nu)$ dependency does not change; the values of the dielectric permittivity of the initial and 1% vol. samples do not change with increasing frequency, while the ϵ' values of the 3% and 5% vol. nanocomposites decrease as frequency increases. The ϵ' values of the 3% and 5% vol. nanocomposites are 4.1 and 3.81, respectively, at 25 Hz. Only for the 5% vol. nanocomposite does the value of ϵ' become smaller than that of HDPE and other nanocomposites after the frequency increases beyond 1 kHz (2.66 and 2.18). In the thermoelectret composites (HDPE +5% α -SiO₂), the total width of dispersion is also equal to $\Delta\epsilon' = 1.68$.

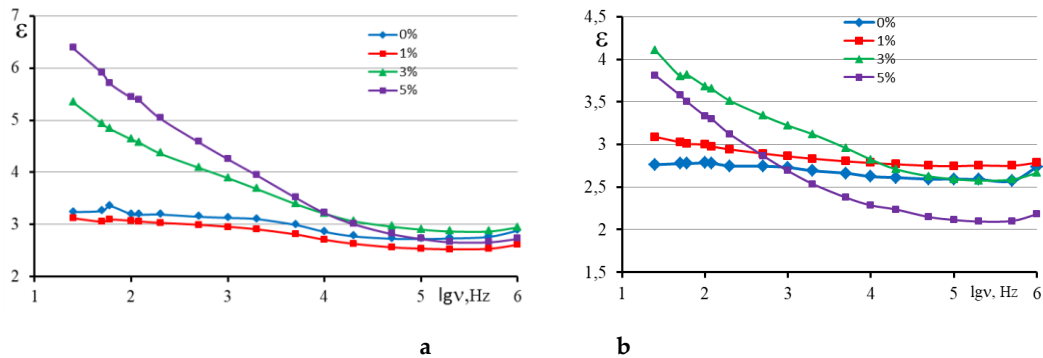


Figure 1. The dielectric permittivity (ϵ) dependence on various frequencies of HDPE and HDPE+ α -SiO₂ initial (a) and thermoelectret (b) composites.

If we compare these graphs, we can see that the parameters of the initial composite samples differ from the values obtained for the thermoelectret composites; the dielectric permittivity of HDPE and HDPE + α -SiO₂ nanocomposites is lower for the thermoelectret nanocomposites. At 25 Hz, the value of ϵ' for the 5% vol. samples of thermoelectrets is 3.81, while for the initial composites, it is 6.38.

In Figure 2, the situation of these samples after irradiation with a dose of ($D=200$ kQr) is shown: it can also be seen that the dielectric permittivity of the initial composites ($\Phi=5\%$) is approximately 8 at 25 Hz; meanwhile, the dielectric permittivity of the thermoelectret is approximately 10, which is a noticeable value.

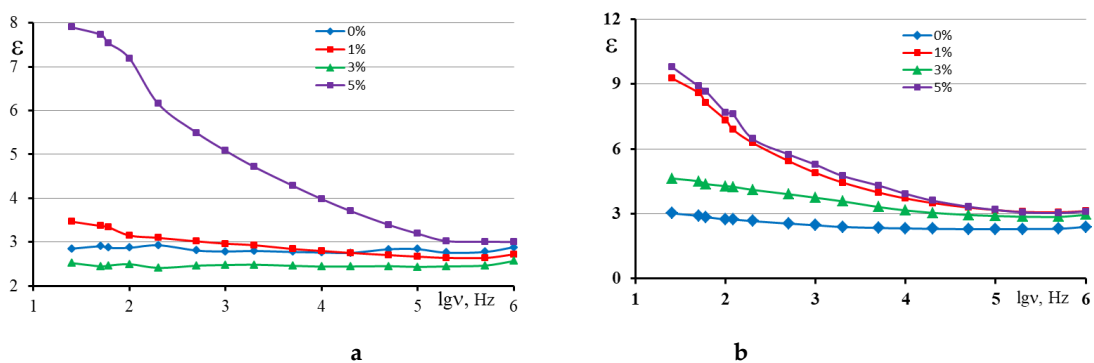


Figure 2. The dielectric permittivity (ϵ') dependence on various frequencies of HDPE and HDPE + α -SiO₂ ordinary (a) and thermoelectret (b) composites after γ -radiation ($D=200$ kGr).

From Figures 1-2(a,b), it can be seen that the effect of γ -radiation absorption dose ($D=200$ kQr) on the dielectric permittivity of HDPE and HDPE + α -SiO₂ composites ($\Phi=0-5\%$) is different. As the volume percentage of the filler and the absorption dose increase, the value of ϵ' increases. This is most noticeable when the volume percentage of the filler is equal to 5%. Thus, as the volume percentage of the filler increases, the radiation resistance of the composite improves.

After irradiation with D=200 kGr, the following changes are observed in the dependency of $\Delta\varepsilon'=f(\nu)$:

1. In the 1% and 3% samples, the value of ε decreases from 5.34 to 2.52, and no frequency dependence is observed across all frequency ranges.
2. After transitioning to the thermoelectret state and irradiation, the ε' values of the 0% and 3% samples increase slightly (from 2.85 to 3.02 for 0%; and from 2.52 to 4.63 for 3%), but no frequency dependence is observed.
3. After irradiation, the value of ε' for the 1% and 5% samples increases at low frequencies (from $\varepsilon' = 7.9$ to $\varepsilon' = 9.79$), then decreases up to 10^5 Hz, followed by stabilization, meaning the stabilization frequency of ε shifts toward higher frequency regions.

Based on the initial analysis of the obtained results, it can be concluded that after irradiation, the increase in ε' and $\text{tg}\delta$ in HDPE and the composites based on it (HDPE + α -SiO₂) after transitioning to the thermoelectret state can primarily be explained by the increase in the degree of polarization of the samples.

Figures 3-4(a,b) show the dependence of the electrical conductivity of initial and thermoelectret polyethylene and the nanocomposites based on it on the volume percentage of the filler before (Fig. 3, a-b) and after (D=200 kGr) (Fig. 4, a-b) γ -irradiation, expressed as $\lg\sigma=f(\nu)$. From the figure (Fig. 3a), it is evident that as the volume percentage of the filler increases, the electrical conductivity (σ) of the composites increases; across all frequency dependencies, the electrical conductivity of the HDPE + α -SiO₂ composites is high. Conversely, after irradiation (D=200 kGr), the electrical conductivity of the thermoelectrets increases (changes); the conductivity of the initial HDPE and HDPE +1% α -SiO₂ composites increases with increasing frequency up to the end of the frequency scale, while in the 3% and 5% volume nanocomposites, this increase continues up to 10^4 Hz and then stabilizes.

In the thermoelectret polymer and nanocomposites (Fig. 3b), the conductivity of the initial (HDPE) and HDPE +1% α -SiO₂ nanocomposites continues to increase significantly, with the conductivity of the 3% and 5% volume nanocomposites being even higher.

After irradiation with a dose of D=200 kGr (Fig.4,a), there are no significant changes in the dependence $\lg\sigma=f(\nu)$ for the HDPE sample, while the conductivity values of the 1% and 5% volume samples are higher compared to HDPE and HDPE +3% α -SiO₂ composites.

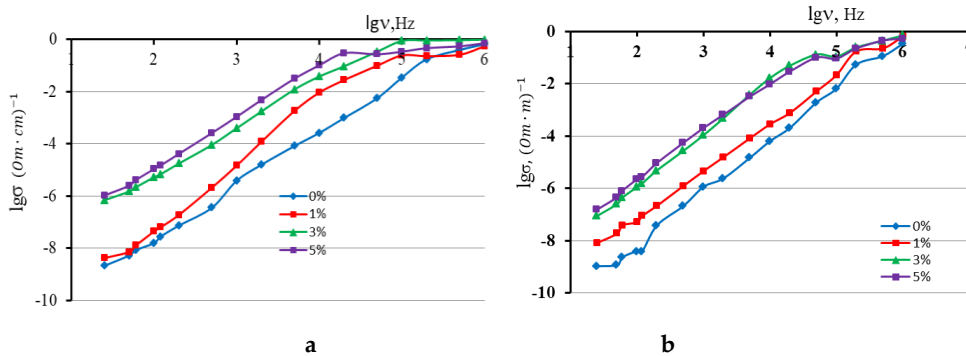


Figure 3. The dependence of electrical conductivity (σ) on various frequencies of HDPE and HDPE + α -SiO₂ initial (a) and thermoelectret (b) composites.

Differences in conductivity are also observed in the thermoelectret polymer and nanocomposites (Fig. 4b), as the conductivity values of HDPE and HDPE +1% α -SiO₂ composites increase from 25 Hz to 10⁶ Hz. In contrast, the conductivity of HDPE +5% α -SiO₂ composites begins to increase from 25 Hz, but after 10⁴ Hz, the increase weakens. During irradiation, the polymer chains break into smaller segments, during which the crystalline regions are disrupted, and the amorphous regions (phases) begin to increase. At high values of the irradiation dose, the polymer chains break, continually improving the amorphous phase and also generating free radicals, which contributes to the increase in electrical conductivity.

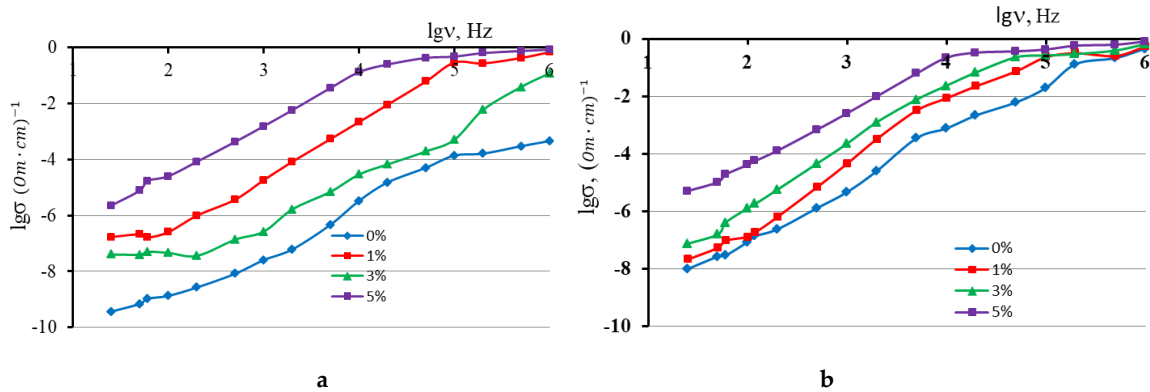


Figure 4. The dependence of electrical conductivity (σ) on various frequencies of HDPE and HDPE + α -SiO₂ ordinary (a) and thermoelectret (b) composites after γ -radiation ($D=200$ kGr).

In Figures 5 (a,b), the dependence of electrical conductivity on the irradiation dose, $\lg \sigma = f(D)$ is shown for HDPE, HDPE + α -SiO₂ initial nanocomposites, and HDPE, HDPE + α -SiO₂ composites that have been transformed into thermoelectrets. From the graph, it can be seen (Fig. 5a) that the electrical conductivity of HDPE and HDPE +1% α -SiO₂ nanocomposites changes little with respect to the dose; however, in the 3% α -SiO₂ nanocomposites, while conductivity decreases at a dose of 100 kGr, it increases relatively at a dose of $D=200$ kGr. The conductivity value in the 5% α -SiO₂ nanocomposite is higher compared to the other composites.

In the thermoelectrets (Fig. 5b), the conductivity values are even higher, especially as both the irradiation dose and the volume percentage of the filler increase, leading to an increase in σ .

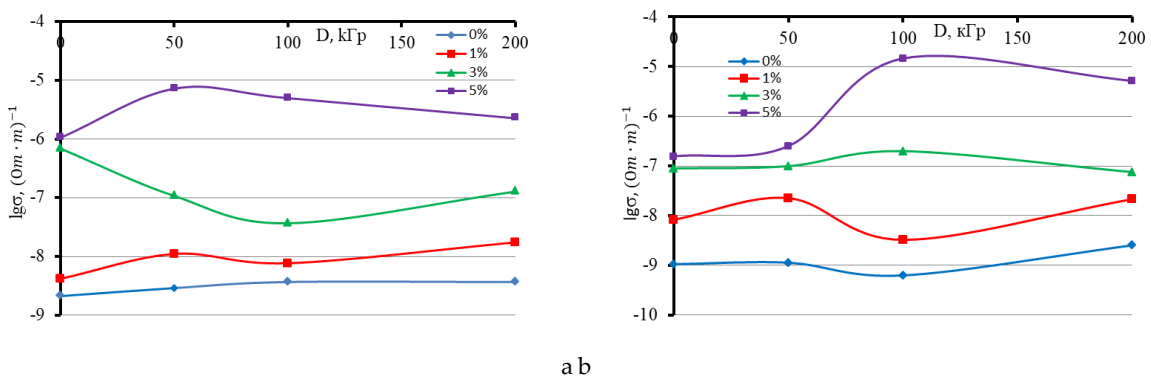


Figure 5. The dependence of electrical conductivity on the dose ($D=0-200$ kGr) for HDPE and HDPE + α -SiO₂ initial (a) and thermoelectret (b) composites.

In thermoelectret nanocomposites, the increase in crystalline regions leads to improved mechanical properties and enhanced chemical resistance. Certain changes occur in polyethylene and composites after γ -radiation. As the irradiation dose increases, defects, unsaturated bonds,

and free radicals generated from the degradation of the polymer chain increase, which contributes to the rise in dielectric permittivity. It has also been established that as the irradiation dose increases, the delocalization of carbonyl groups and charge carriers increases, leading to an increase in dielectric permittivity (ϵ). However, the dielectric permittivity of thermoelectret nanocomposite samples increases significantly.

CONCLUSION:

The effect of γ -irradiation on the electrophysical properties of YSPE+ α -SiO₂ nanocomposites with various concentrations has been studied. Based on the initial analysis of the obtained results, it can be concluded that after irradiation, YSPE and the composites derived from it (YSPE+ α -SiO₂) transition to a thermoelectret state, which is characterized by an increase in ϵ and $\text{tg}\delta$. This increase can primarily be attributed to the enhancement of the polarization degree of the samples and the growth of electrical conductivity. After irradiation, a slight increase in the ϵ value for the 1% and 5% samples at low frequencies is observed, followed by a shift in the stabilization frequency of ϵ toward higher frequency regions.

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